Novel Polyimide Battery Separator Imbibed with Room-Temperature Ionic Liquids

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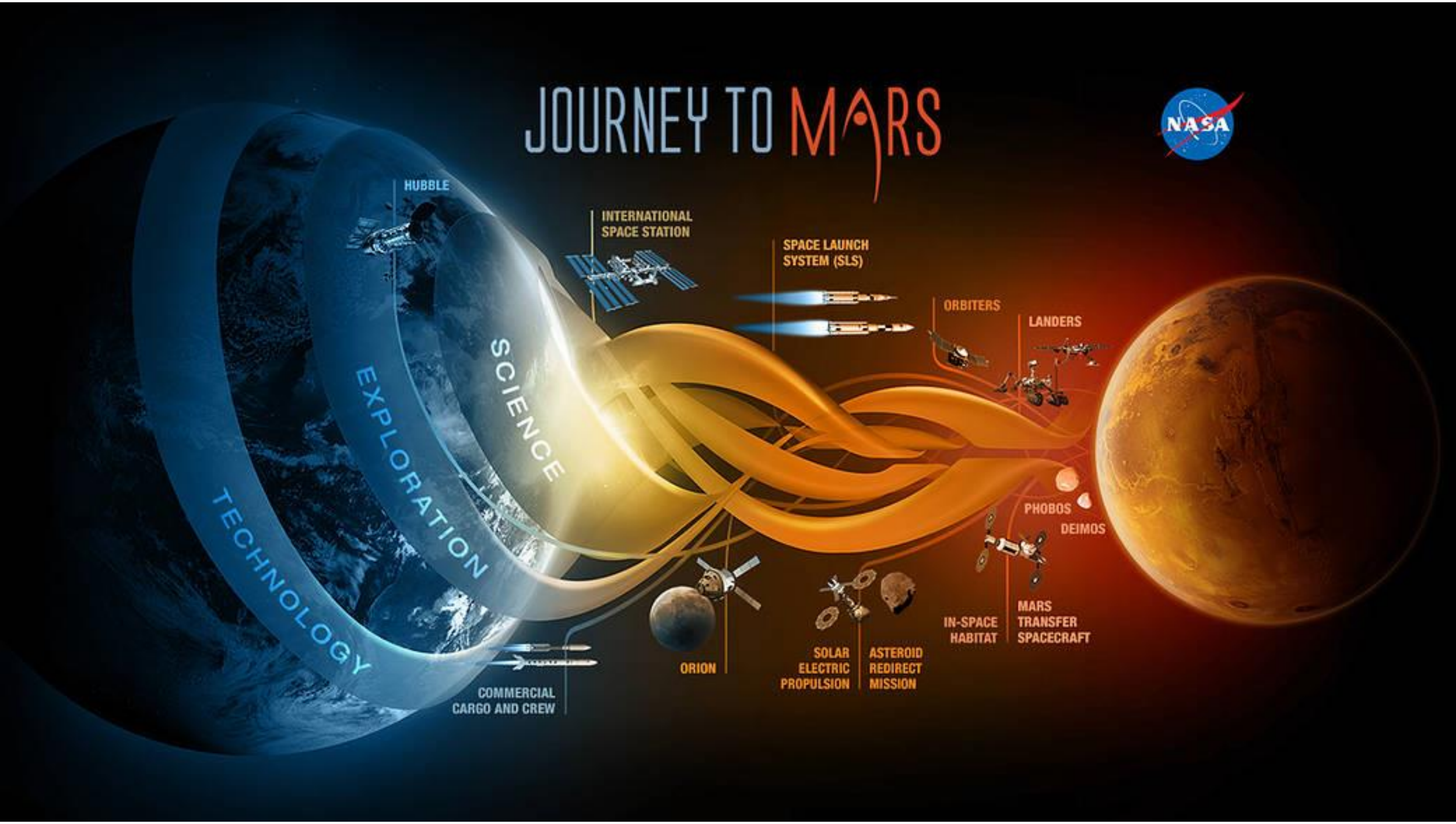
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Multifunctional Energy Storage to Improve Efficiency

Enable hybrid electric propulsion for commercial aircraft by coupling load-bearing structure with energy storage

Challenges

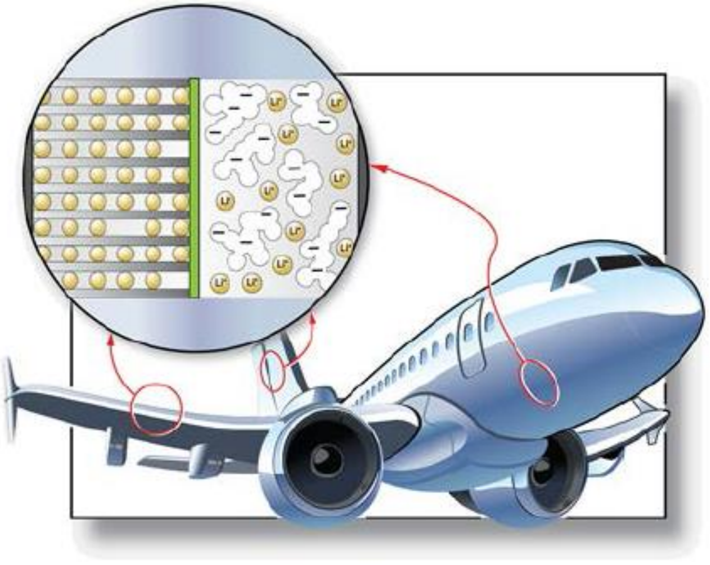
- Producing a structure capable of bearing weight and resisting forces associated with flight

Risks

- Current Li-Ion battery technology utilizes flammable components

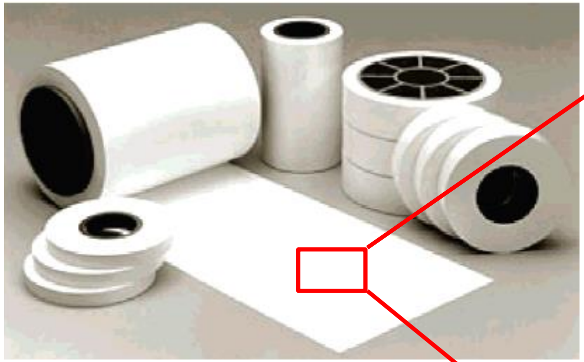
Goals

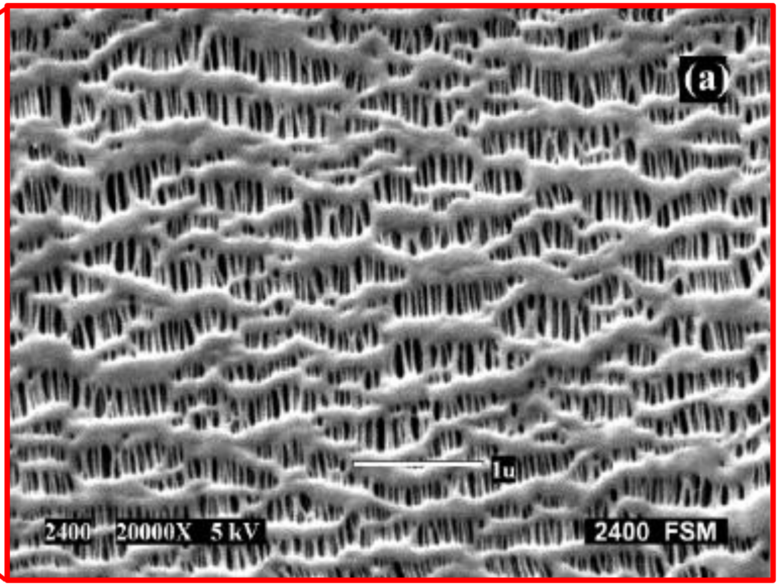
- Develop a separator/electrolyte system which possesses sufficient ionic conductivity with non-flammability



Hybrid electric aircraft with multifunctional storage could reduce emissions by 80% and fuel consumption by 60%

Polyolefin Separators used in Li-Ion Batteries



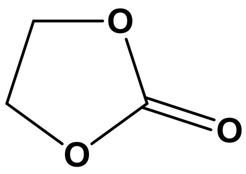


Separator/Properties	Celgard 2730	Celgard 2400	Celgard 2325	Asahi Hipore	Tonen Setela
Structure	Single Layer	Single Layer	Trilayer	Single Layer	Single Layer
Composition	PE	PP	PP/PE/PP	PE	PE
Thickness (μm)	20	25	25	25	25
Porosity (%)	43	40	42	40	41
Melt Temp. (°C)	135	165	135/165	138	137

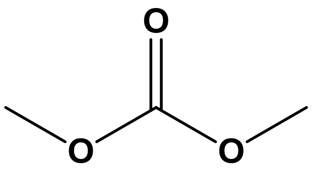
- Polyethylene and polypropylene are among the most flammable polymers
- Limited number of electrolytes wet the polyolefins

Electrolytes Currently Used in Li-Ion Batteries

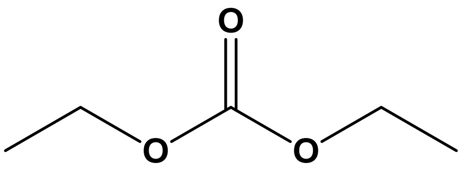
ethylene carbonate



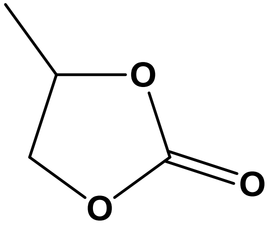
dimethyl carbonate



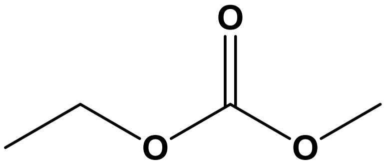
diethyl carbonate



propylene carbonate



ethyl-methyl carbonate



- Current Li-ion technology uses combinations of carbonates as the electrolyte
- The ionic conductivity of polyolefin separators imbibed with carbonates is ~10^{-2} – 10^{-3} S/cm
- However, the carbonates are highly flammable

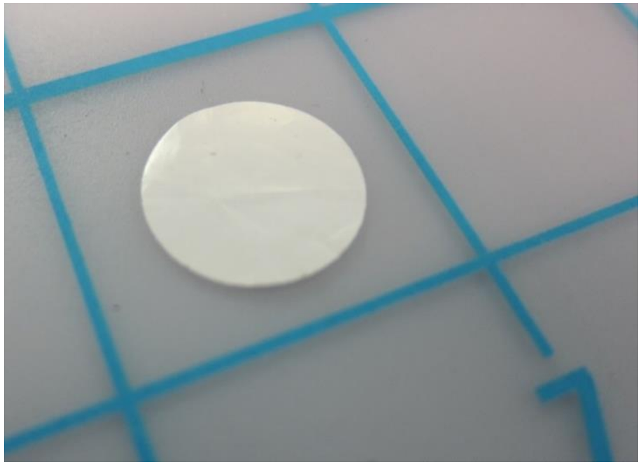
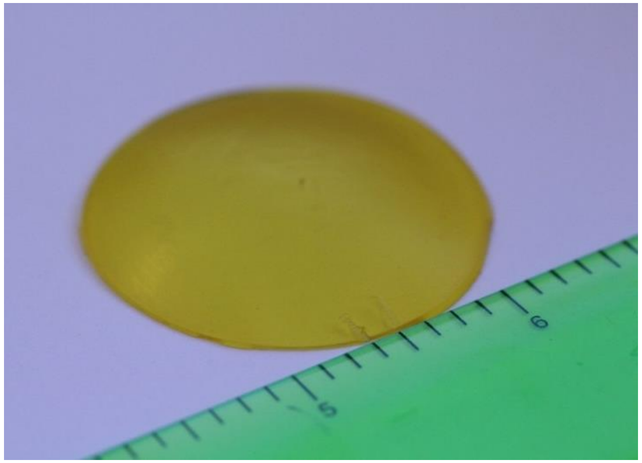
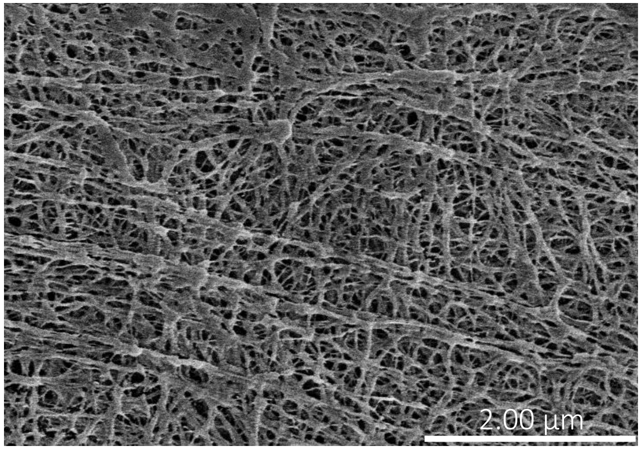
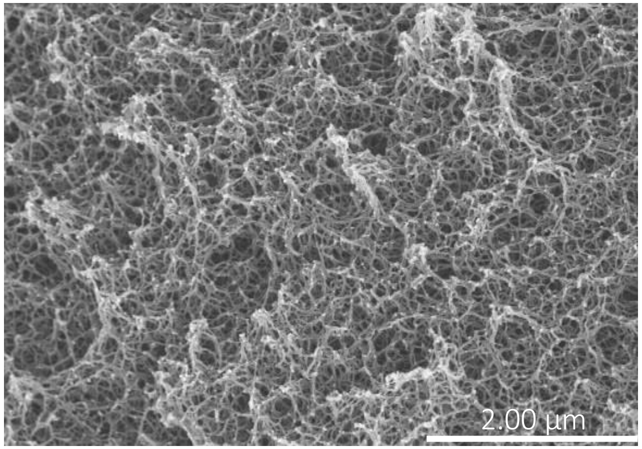
Separator Requirements for Li-Ion Batteries

Separator Requirements

- Electronic insulator
- Minimal electrolyte resistance
- Mechanical and dimensional stability
- Sufficient mechanical strength to allow manufacture
- Chemical resistance to degradation by electrolyte
- Readily wetted by electrolyte
- Porosity of at least 40%
- Uniform in thickness
- Thermal stability
- Shut-off temperature

Photo courtesy Cnet.com

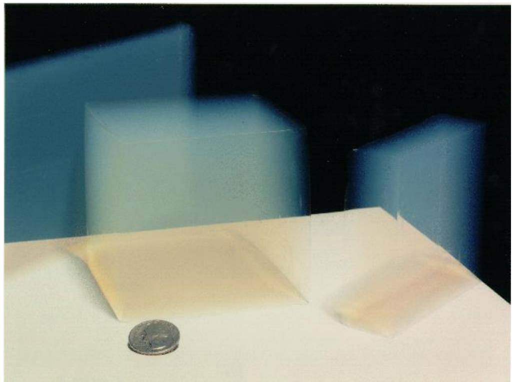
Comparison of Commercial Separator and PI Aerogel

Celgard© PE Separator	Polyimide Aerogel
	
	

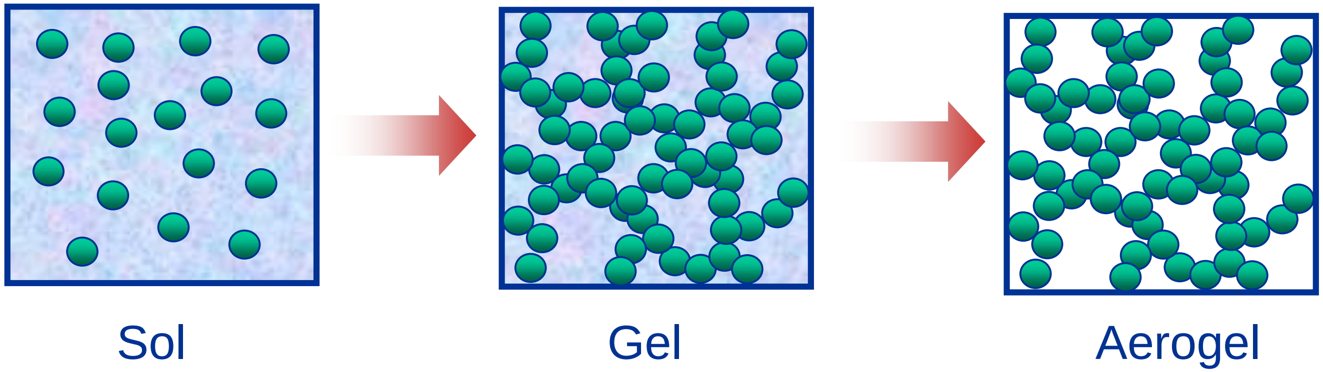
What are Aerogels?

Aerogels are a class of porous solids which exhibit many extreme properties which originate from a nanoporous skeletal architecture

- Highly porous solids made by drying a wet gel without shrinking
- Pore sizes extremely small (typically 10-40 nm)—makes for very good insulation
- 2-4 times better insulator than fiberglass under ambient pressure, 10-15 times better in light vacuum
- Invented in 1930's by Prof. Samuel Kistler



Silica Aerogel Monoliths

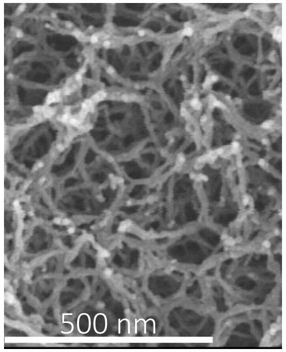


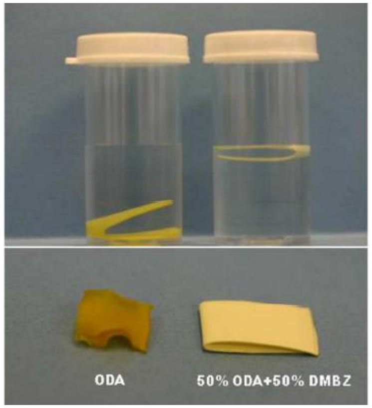
Development of Polyimide Aerogels

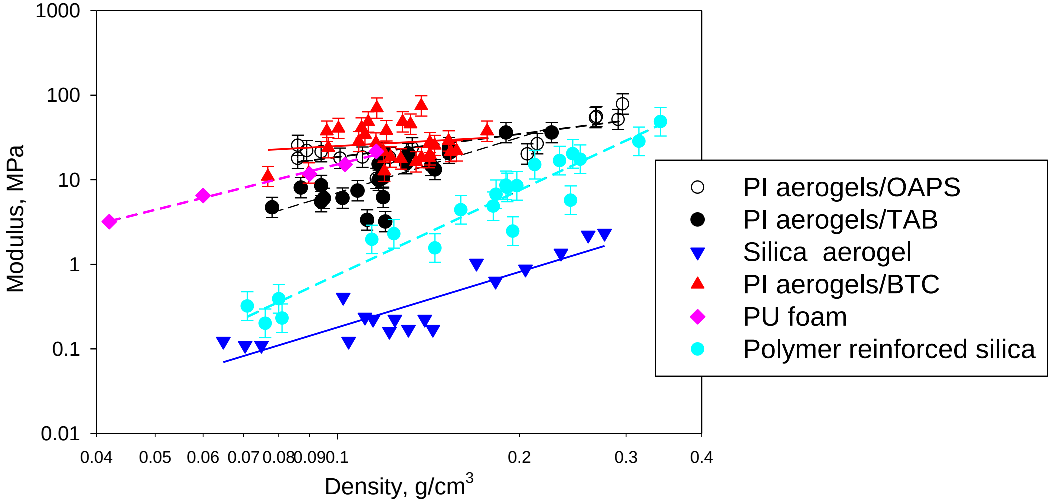
- Over 50 combinations of diamines and dianhydrides in the polymer backbone have been characterized
- Multiple cross-linkers have been investigated
- Properties dependent on backbone chemistry

Typical properties

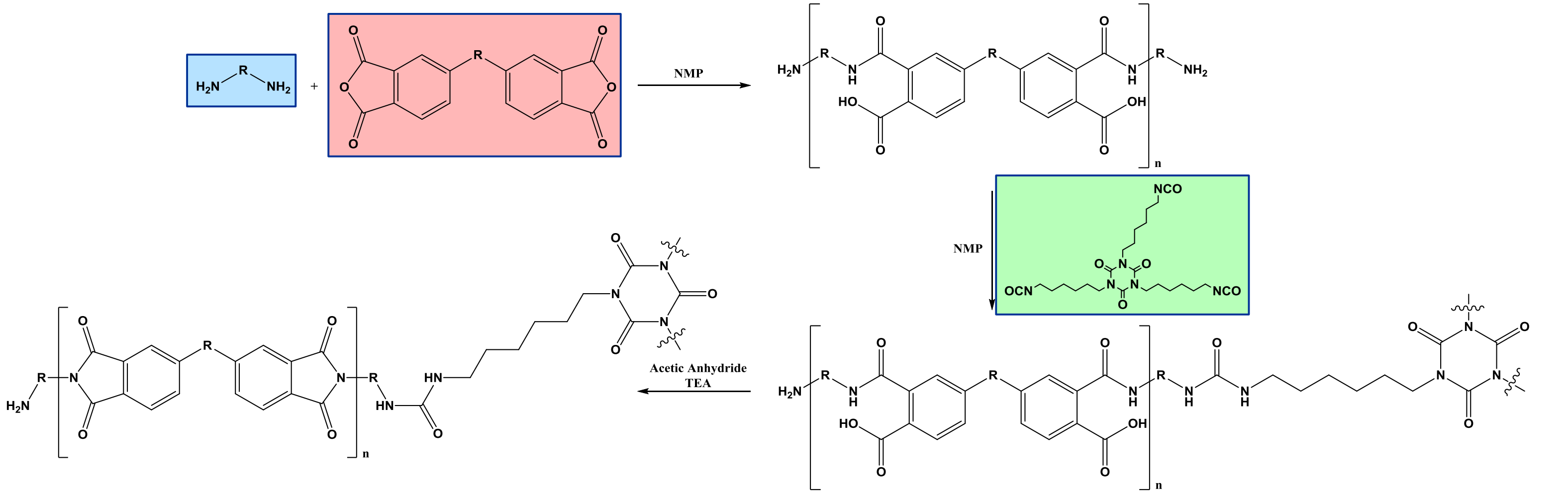
- High porosity (>85%)
- Pore size 10-40 nm
- Open-cell fibrillar architecture
- High thermal stability
- Char-forming, non-flammable
- Tunable hydrophobicity
- Tunable mechanical properties
- Can be cast into flexible thin films

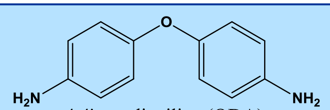


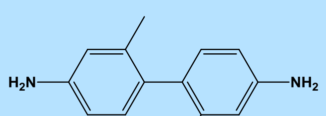


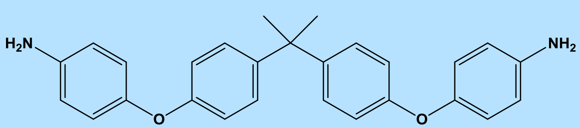


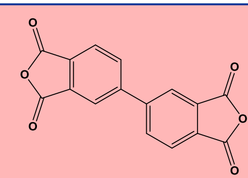
General Polyimide Reaction Scheme

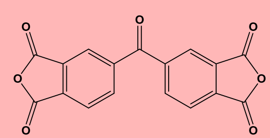


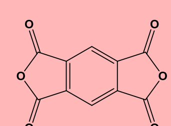

4,4'-oxydianiline (ODA)

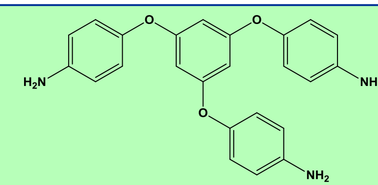

2,2'-dimethylbenzidine (DMBZ)

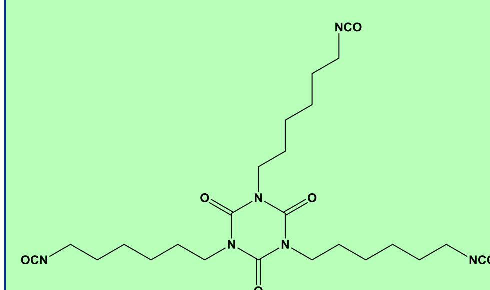

2,2'-bis(4-[4-aminophenoxy]phenyl)propane (BAPP)


3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA)

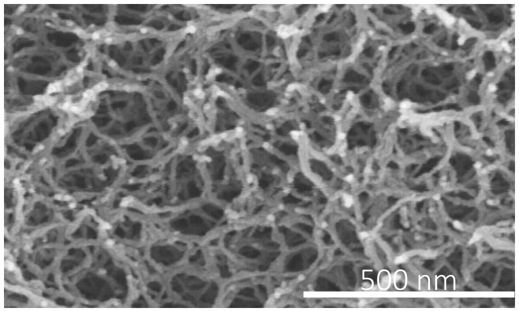

3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA)

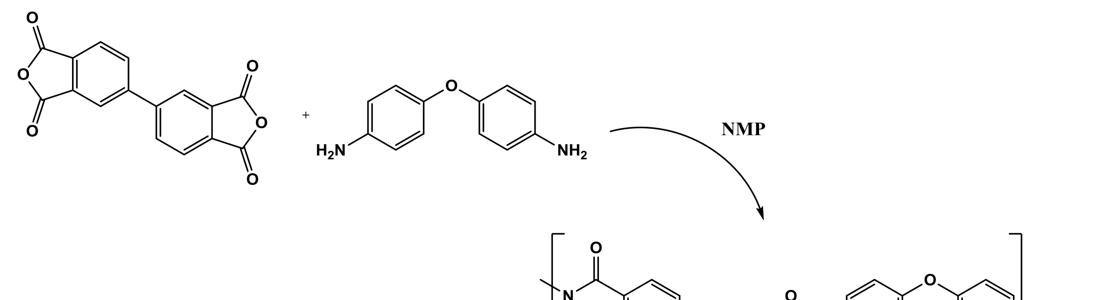
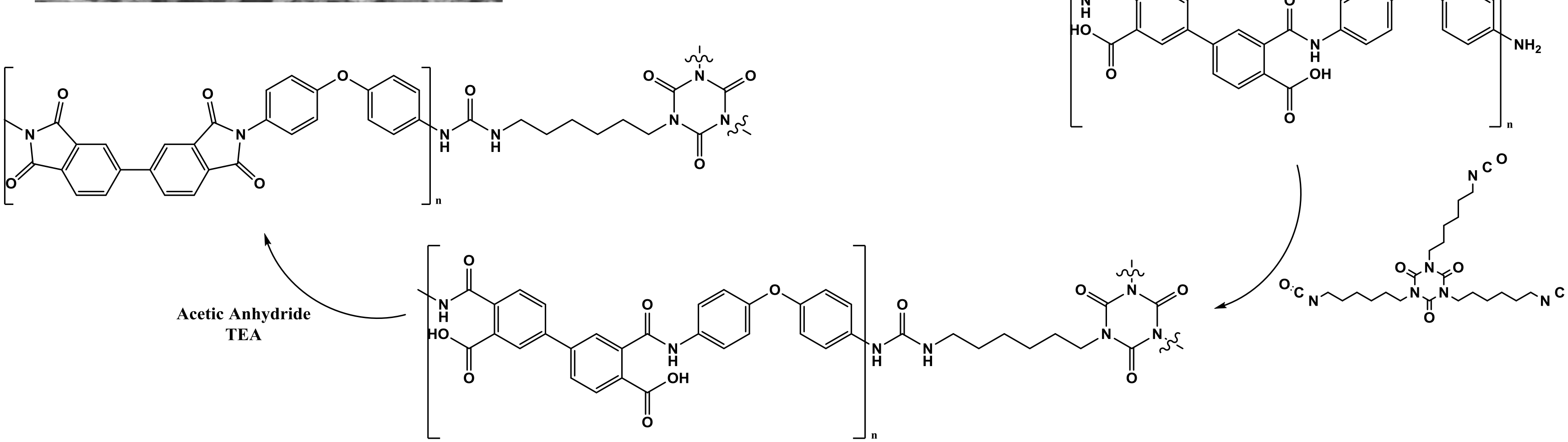

Pyromellitic dianhydride


1,3,5-tris(4-aminophenoxy)benzene (TAB)


N3300A

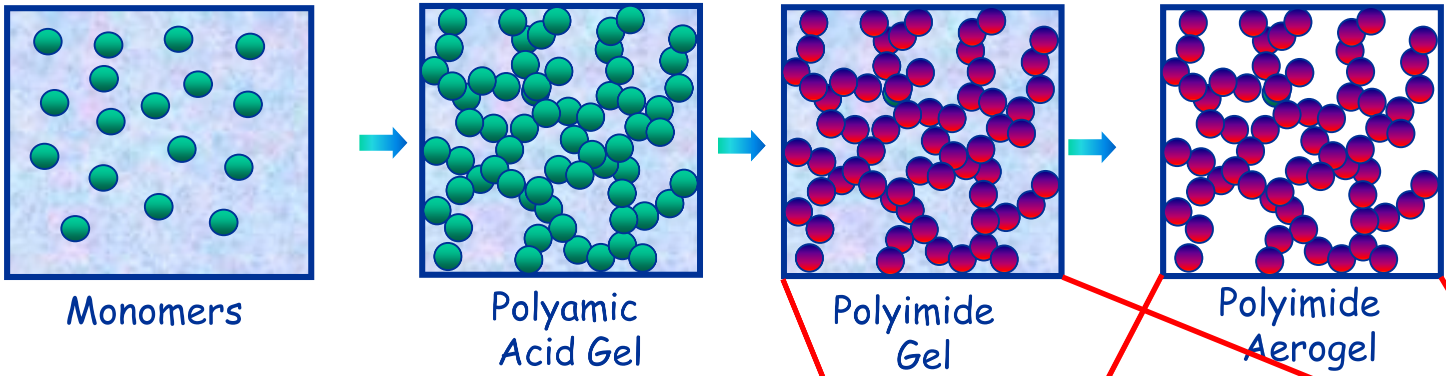
Down Selection to ODA-BPDA-N3300A

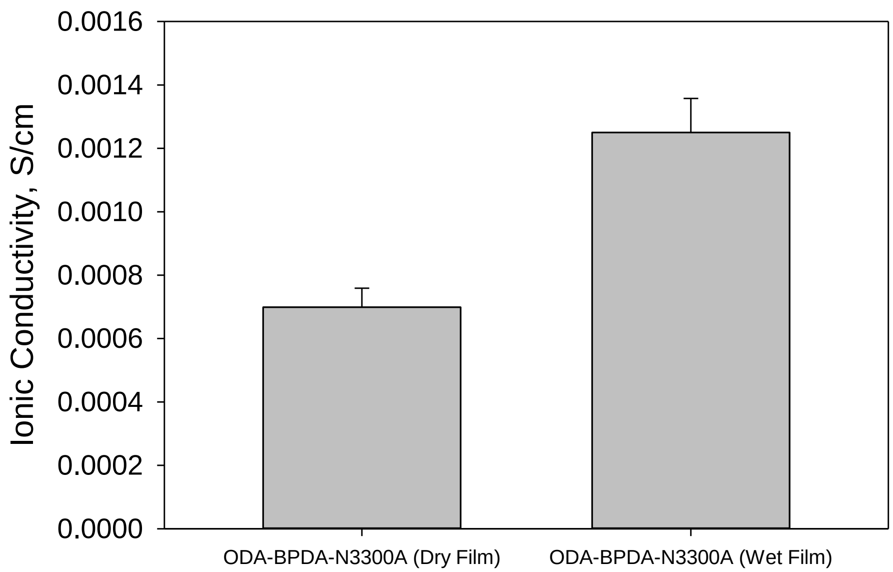


- Many polyimide backbone chemistries were synthesized and characterized
- Several factors were considered in down selection: film forming, mechanical strength, porosity
- ODA-BPDA-N3300A formed thin, mechanically robust films, with porosities of 93%

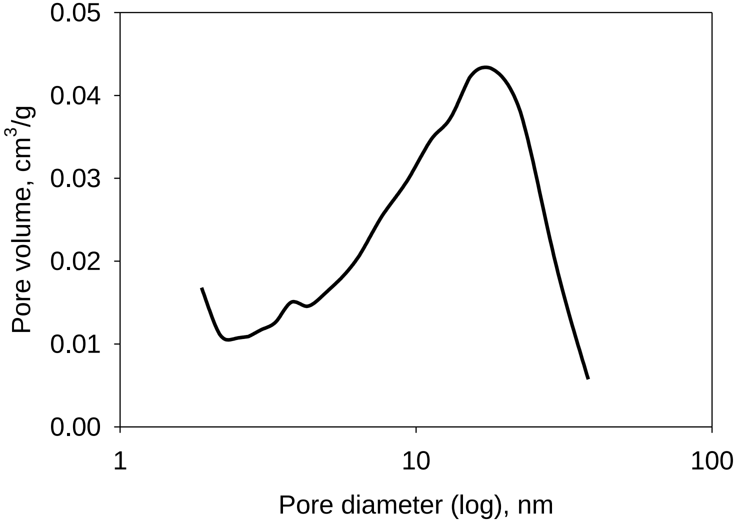
Higher Ionic Conductivities for Films that have not been Dried

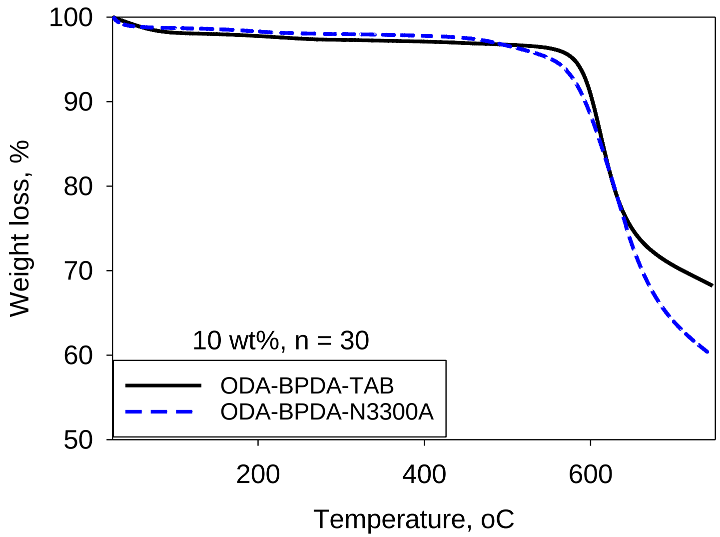


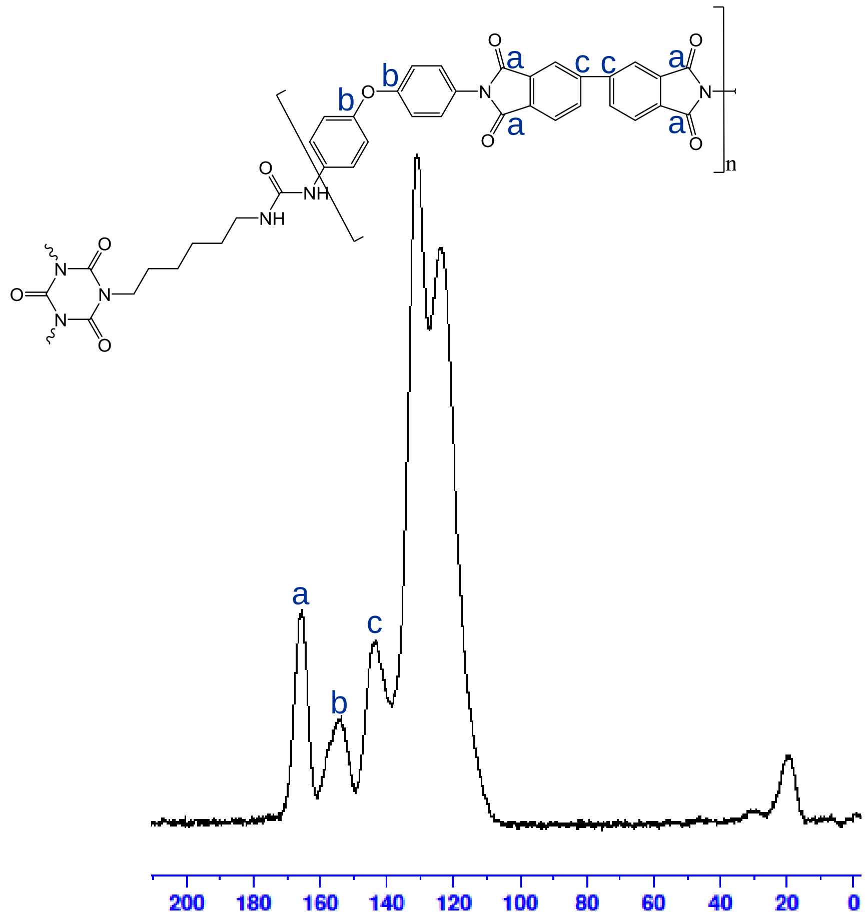


With 1-methyl-1-propylpyrrolidinium TFSI, conductivity is half when film is dried first

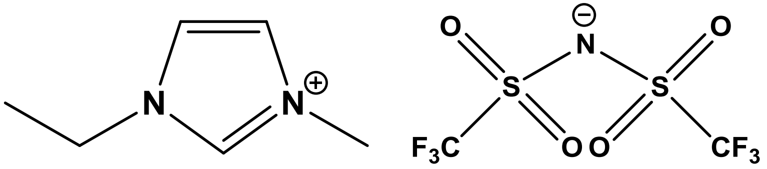
Physical Characteristics of ODA-BPDA-N3300A PI





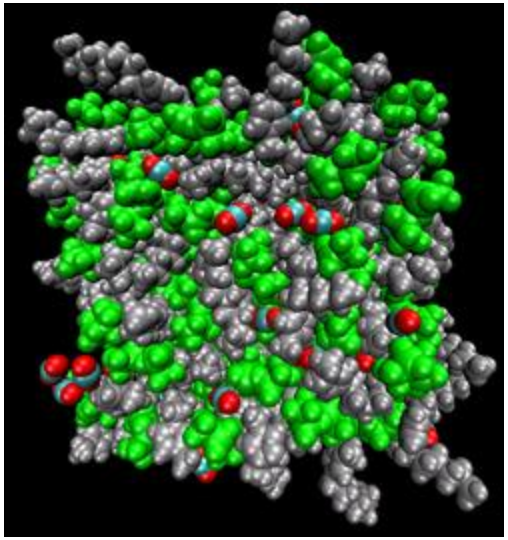


Properties of Ionic Liquids



1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

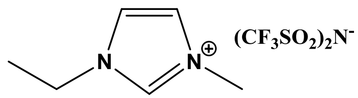
- Room temperature ionic liquids (RTILs) consist of an asymmetric organic cation and a bulky anion with delocalized charge
- RTILs are nonvolatile and nonflammable
- Wide range of viscosities
- Highly polar
- Tunable miscibility
- Highly thermally stable – imidizolium cation stable above 300 °C
- Most RTILs do not wet polyolefins



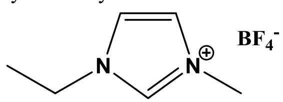
Courtesy U.S. Department of Energy

Screening Study of RT Ionic Liquids

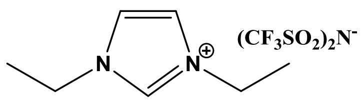
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide



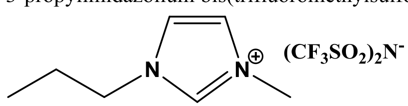
1-ethyl-3-methylimidazolium tetraborate



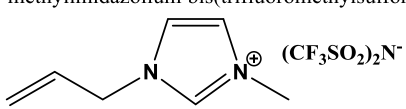
1,3-diethylimidazolium bis(trifluoromethylsulfonyl)imide



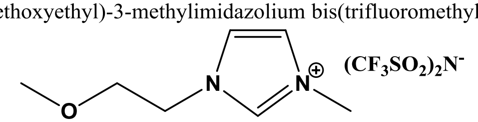
1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide



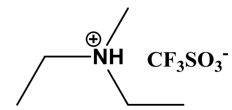
1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide



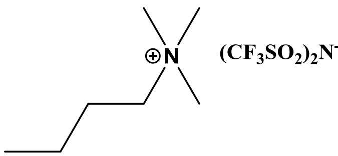
1-(2-methoxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide



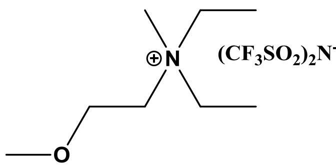
diethylmethylammonium trifluoromethanesulfonate



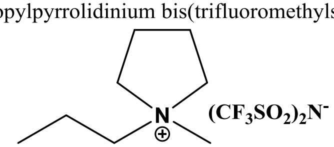
butyltrimethylammonium bis(trifluoromethylsulfonyl)imide



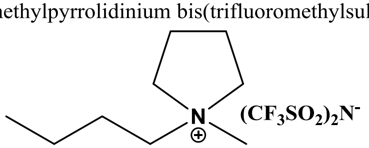
N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl)imide



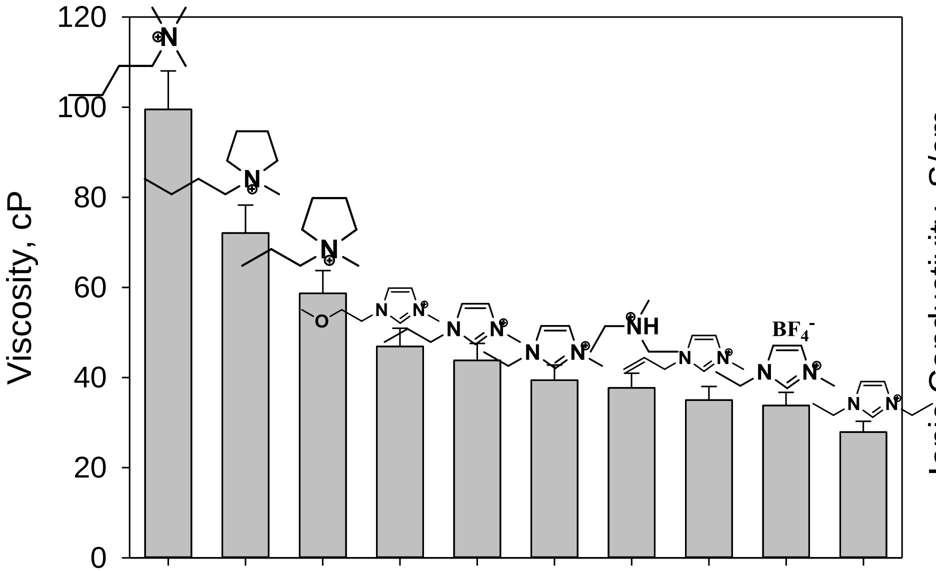
1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide

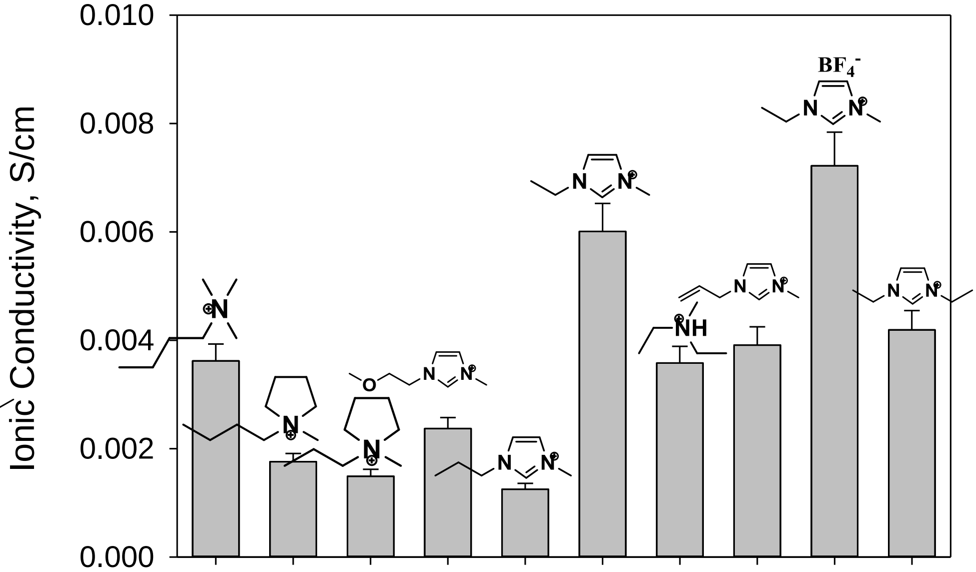


1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide



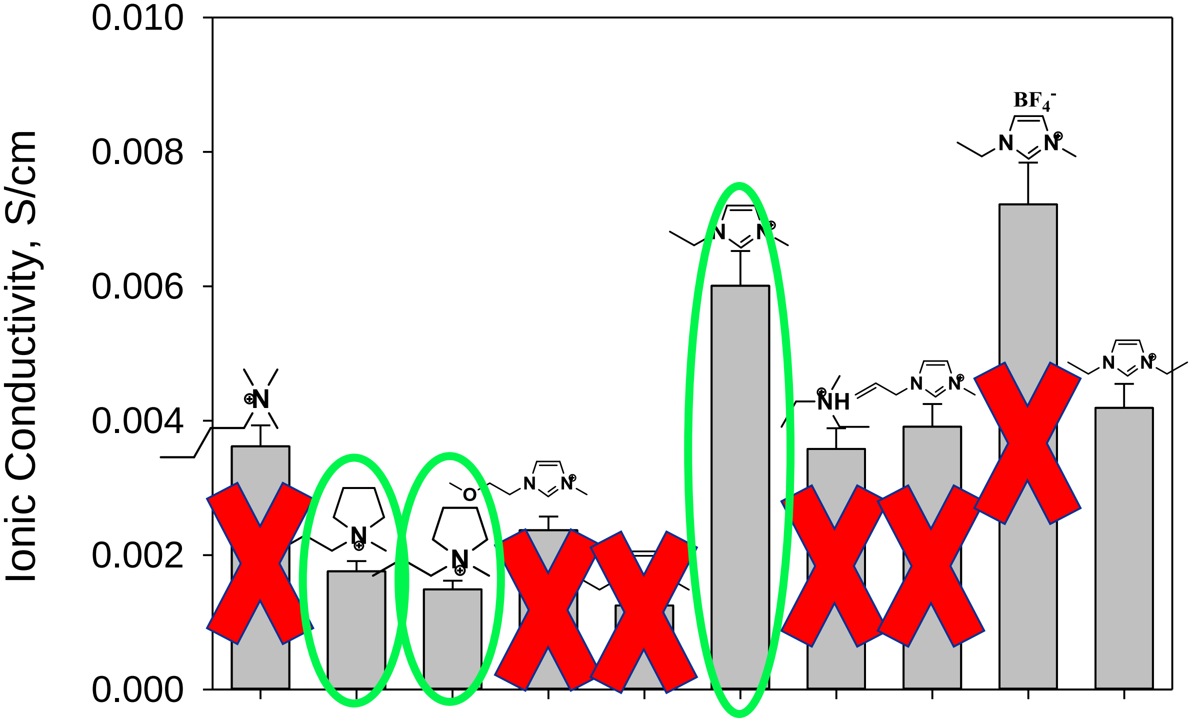
Viscosity Influenced but Did not Determine Conductivity





- All ILs use TFSI as the anion, except one which uses BF_4^-
- Viscosity has an effect on conductivity, but not the only important factor
- Several ILs showed electrochemical instabilities or compatibility issues with anode/cathode

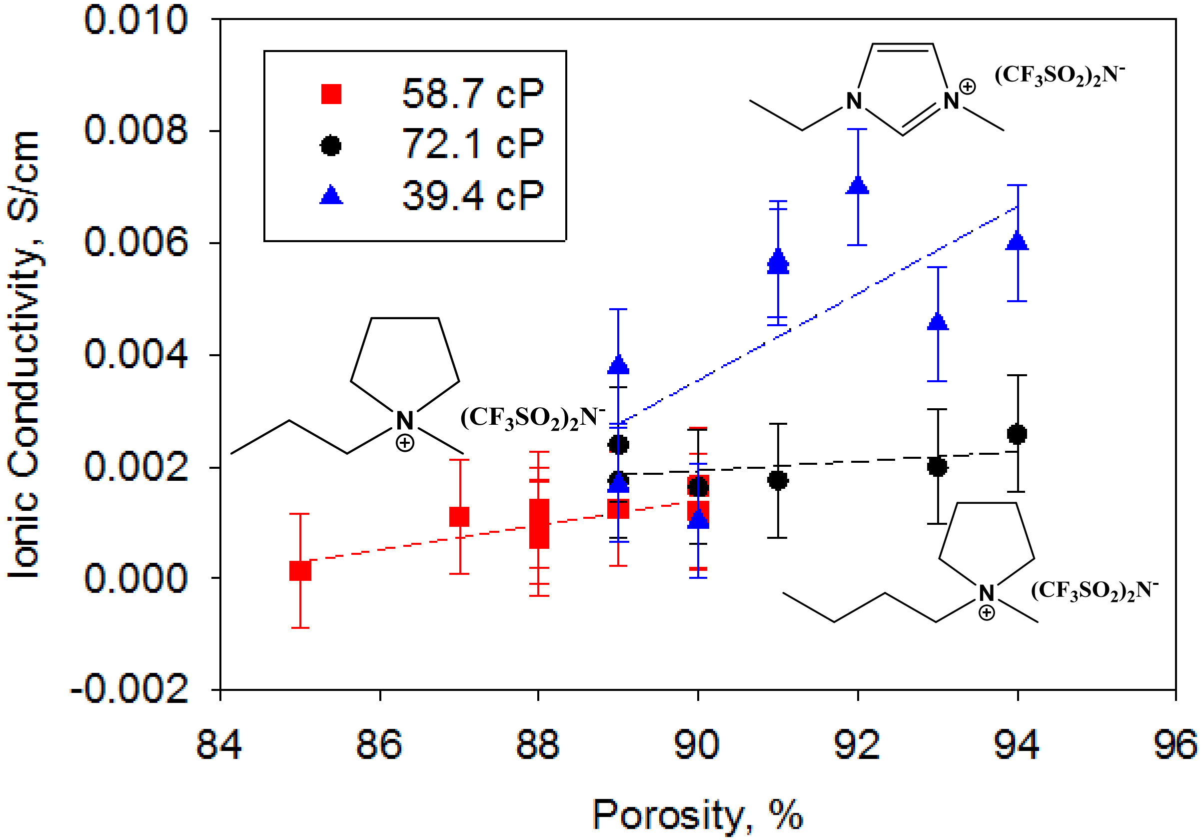
Down Selection to Three ILs



- The ammonium compounds eroded the current collectors
- 2-methoxyethyl imidizolium and 1-allyl imidizolium are unstable electrochemically
- 1-ethyl-3-ethyl imidizolium BF_4^- yellowed and degraded in the presence of the carbon cathode
- The propyl imidizolium possessed a low conductivity

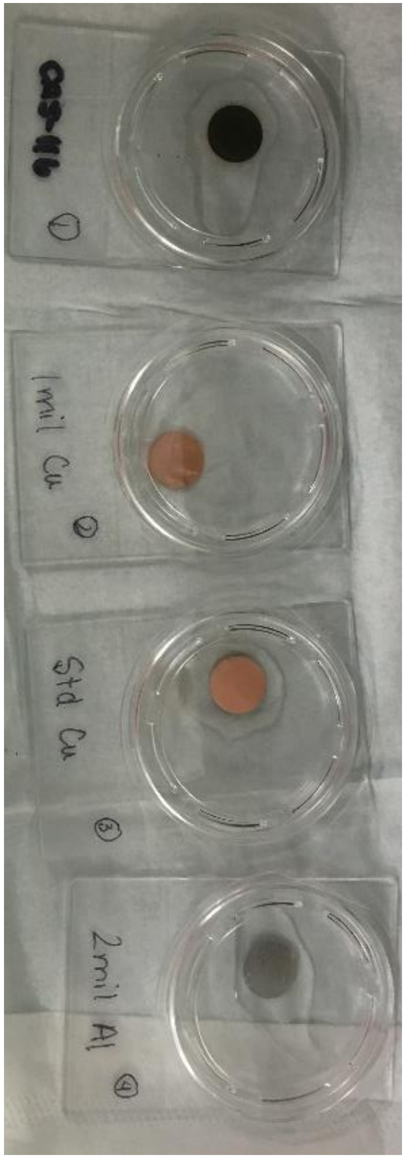
- The 2 pyrrolidinium compounds displayed the highest degree of electrochemical stability
- EMIM TFSI showed the highest conductivity of the stable compounds
- The diethylimidizolium compound was more expensive and less conductive than EMIM TFSI

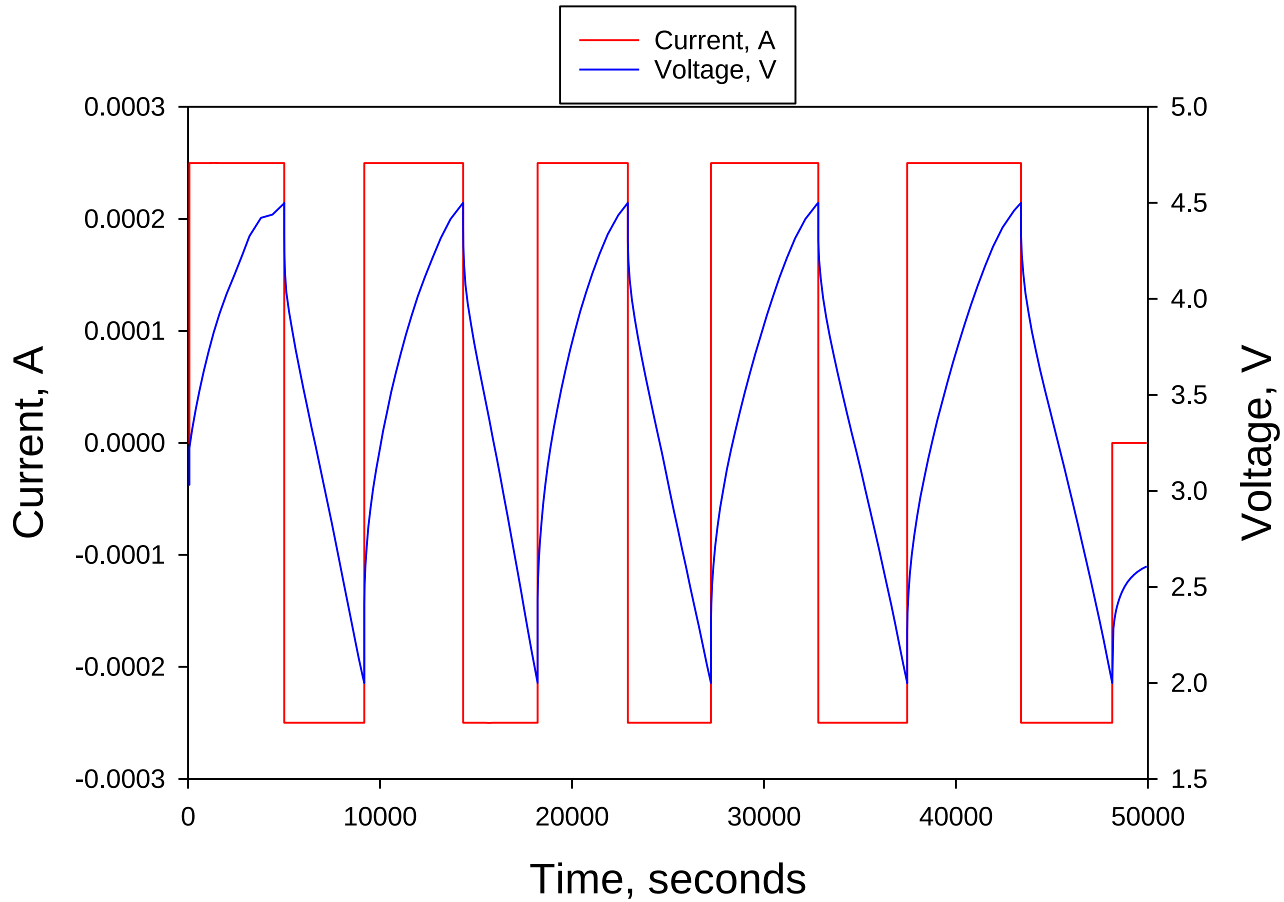
Ionic Conductivity Increases with High Porosity and Low Viscosity



- The porosity of the separator had a large influence on the ionic conductivity
- ODA-BPDA-N3300A produced the highest porosity samples
- Viscosity influenced conductivity when the porosity was the same

PI/EMIM TFSI Gel Separator Cycled for 14 Hours





- EMIM TFSI is stable in the presence of the aluminum cathode and copper anode – no visible discoloration or reaction

PI/EMIM Gel Separator is Nonflammable Under Direct Contact with Flame

Conclusions and Future Work

- **A separator based on a porous polyimide gel imbibed with an ionic liquid has been demonstrated**
- **Ionic conductivity increased as a function of increasing porosity and decreasing ionic conductivity**
- **The separator was stable in the presence of the copper anode or aluminum cathode over 14 hours cycling**
- **The separator was not flammable under direct exposure to flame**

Acknowledgements

- Dr. Mary Ann Meador
- Dr. Baochau Nguyen
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- Dr. Liming Dai
- Stephanie Vivod
- Dan Scheiman
- Linda McCorkle
- Dr. Vadim Lvovich
- LMN Branch

Empirical modeling produces response surfaces

Variables

- X_1 = Total % Polymer (7%, 8.5%, 10%)
- X_2 = n-Value (20, 30, 40)
- X_3 = Mole % Diamine (0%, 25%, 50%)

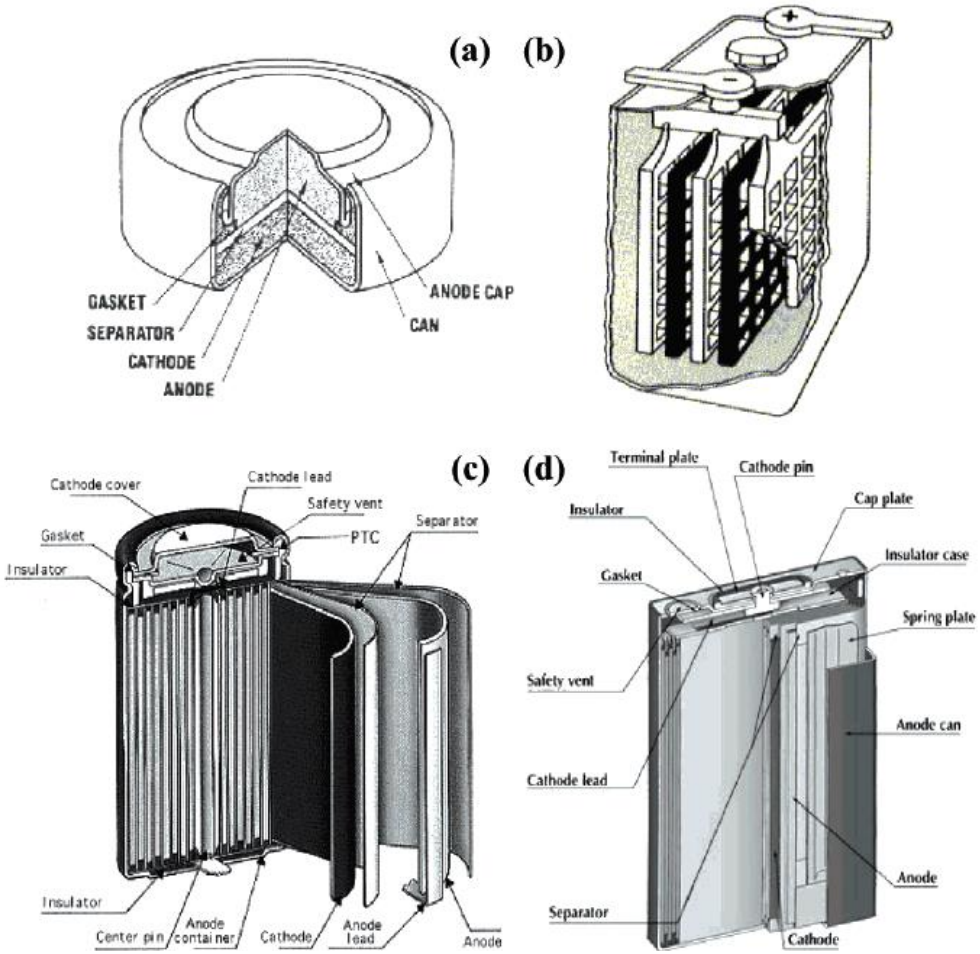
Multiple Linear Regression Analysis

$$Response = C + C_2X_1 + C_3X_2 + C_4X_3 + C_5X_1^2 + C_6X_2^2 + C_7X_3^2 + C_8X_1X_2 + C_9X_1X_3 + C_{10}X_2X_3$$

Analysis of Variation (ANOVA Table)

- Backward Stepwise Regression Analysis
- Statistically insignificant terms are removed from model sequentially until only significant terms remain ($p < 0.1$)

Typical Battery Configurations



(a) button cell; (b) stack lead-acid; (c) spiral wound cylindrical lithium-ion; (d) spiral wound prismatic lithium-ion